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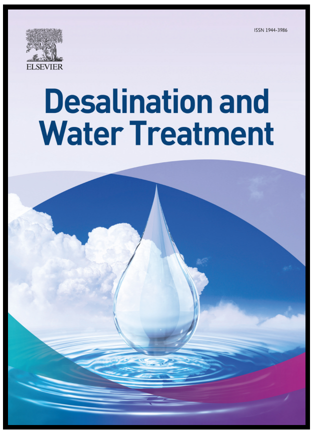

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Resource recovery and water reclamation from acid mine drainage: Market analysis, industry trends, and future research directions

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Abstract

Acid mine drainage (AMD) is a highly recalcitrant wastewater that is typically generated from coal and metal mining activities and contains elevated levels of (heavy) metals and sulphates, along with rare earth elements (REEs) and radionuclides in some instances. This review seeks to elucidate AMD's physicochemical characteristics and resource recovery avenues that can underpin circularity and introduce the waste-to-resource paradigm. Opportunities for major metals (e.g., iron (Fe) aluminum (Al), and manganese (Mn)) and critical minerals, such as v cobalt (Co), nickel (Ni), and notably rare earth elements (REEs), recovery, along with other minor constituents such as radionuclides were explored. Other valorization avenues such as sulfates transformation to sulfuric acid and recovery and water reclamation were further explored. The techniques for resource recovery from AMD, such as precipitation, adsorption, solvent extraction and ion exchange, were discussed, as well as possible industrial uses of the recovered materials (e.g., coagulants, adsorbents, pigments and catalysts). AMD beneficiation and valorization can minimize the ecological footprint of AMD and reduce virgin resource extraction, such as REEs, while water reclamation can provide water security in water-scarce countries. The recovered resources can provide an important revenue stream, via offsetting treatment costs and even making the process self-sustainable due to the high value of certain products. For example, the REEs global market in 2023 was USD$5.9 billion and is expected to reach USD$14.2 billion by 2033, with a compound annual growth rate (CAGR) of 12%, thus denoting that recovering REEs from AMD could be profitable, while it also reduces mining requirements and associated environmental impacts. Finally, knowledge gaps in terms of recoverability, along with their challenges and prospects and avenues for further research, were also distilled.

Keywords:

wastewater treatment; recovery and beneficiation of valuable minerals; wastewater and sludge valorisation; circular economy; ecological and environmental sustainability; from waste to wealth and waste hierarchy; market analysis.

1 Introduction

The use of virgin materials in production, manufacturing, wastewater treatment, and environmental remediation puts immense pressure on natural resources [1]. Specifically, rapid population growth has intensified resource demand, which far exceeds its sustainable supply [2]. This unsustainable consumption pattern ultimately leads to natural resource depletion and environmental damage, as a direct result of anthropogenic activities that seek to cater for the daily needs of humanity [3, 4]. Not only this, but such activities often result in the generation of hazardous effluents and emissions, thereby introducing toxic species into water resources and land [5]. Such pollutants pose a risk to humans and aquatic and terrestrial life due to the carcinogenic, mutagenic, and teratogenic effects with which they are associated [4].

One such hazardous effluent is acid mine drainage (AMD), which emanates from mining activities, typically during gold and coal mining where pyrite (FeS_2) is oxidized in the presence of water and acidophilic iron-oxidizing bacteria [6]. Specifically, the formation of AMD occurs in an abiotic environment; however, microorganisms, such as bacteria and archaea, can accelerate the breakdown of metal ions in the AMD [7]. Extremophiles, which are the microorganisms taking part in the AMD generation, can endure high acidity; however, their abundance is limited by the availability of oxygen and water [8]. As a result, acidity is produced, thus lowering the pH of the aqueous medium [9]. The high acidity [10] and sulphate content, along with the elevated levels of (heavy) metals [11], radioactive nuclides, and salts in raw AMD, can greatly affect ecosystem quality [12] and cause detrimental effects to living organisms and human health [13]. For example, respiratory problems, skin burns, eye damage, gastrointestinal distress, kidney and liver damage, and even cancer have been associated with exposure to AMD [14].

Traditionally, focus has been placed on conventional pollution control, in the AMD case through neutralization. However, technological advances and particularly the introduction of circular economy, waste hierarchy, and other concepts, such as treating waste with waste, zero-liquid discharge (ZLD), and closed-loop systems (CLS) have led to a paradigm shift, viewing AMD as an important resource rather than as a waste. This is owed to the large number and high concentrations of valuable metals, sulphates, and rare earth elements (REEs) that it contains [15], and, of course, to the water itself. To this end, various processes and techniques have been examined for resource recovery and utilization from AMD [16]. Their efficiency depends on the local characteristics of the AMD, such as pH and concentrations of dissolved species, as well as the target mineral(s) to be recovered, while cost is also important. Here, an in-depth evaluation of the recent advances, emerging trends, and opportunities in resource recovery, valorization, and beneficiation from real AMD is provided. Focus is also placed on the market analysis of REE recovery from AMD.

Interrelations with circular economy and sustainability are also explored, along with water security contributions, focusing on the paradigm shift from the traditional neutralization and pollution control approaches to beneficiation (metals/minerals recovery) and valorization, i.e., value creation through clean water reclamation and/or by converting recovered products into marketable products. We make a distinction for beneficiation, which often refers to the processing of solid waste rocks or tailings to further extract targeted metals/minerals from AMD, which, apart from dissolved metals from the source rock, can include additional metals (due to its low pH) from downstream sources. As such, AMD beneficiation here refers to the recovery of metals/minerals that were included in source rock as well as from additional sources. The recovered metals/minerals can be used for different applications as they are, such as treating waste with waste, or being further processed and valorized.

2 Metals and minerals content in acid mine drainage

Depending on the geochemical composition of the mineral ore and geology of the mining area, AMD typically contains major metals, such as iron (Fe), aluminium (Al), calcium (Ca) and manganese (Mn), along with smaller contributions of other metals and metalloids, such as arsenic (As), cadmium (Cd), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb) and zinc (Zn) [17]. As such, AMD is particularly enriched in metals and metalloids [18], often many orders of magnitude above prescribed limits, such as the South African National Standards for Drinking Water (SANS241), and guidelines, such as those of the World Health Organisation (WHO), thus threatening human health and the environment if not treated [16]. It can also contain elevated levels of REEs [18], rendering it an important REE secondary source that is attracting increasing attention [19]. This is because when REEs are mined, copious amounts of toxic and radioactive waste are generated since ore deposits typically consist of uranium (U) and thorium (Th), both highly radioactive [20]. Additionally, the substantial use of chemicals for their recovery, as well as the generation of harmful tailings, presents further environmental concerns. Therefore, AMD can serve as an alternative REEs source, particularly for cerium (Ce), lanthanum (La), and neodymium (Nd), which are three important REEs in high demand [21], while REEs and critical minerals (e.g., cobalt (Co), Ni, and Mn) recovery from AMD can potentially by economically viable [22]. Thus, apart from common metals and minerals, it would be useful and environmentally sustainable to recover also REEs from AMD, as this would decrease the demand for REEs mining and help monetize AMD into valuable by-products that can generate revenue to offset remediation costs and possibly even generate profit [23, 24].

For this reason, here, we performed a systematic search using the Scopus database and then extended the search to Google Scholar to identify relevant literature about AMD metals and minerals content with a specific focus on valorization and beneficiation. Furthermore, AMD is encountered in many different mining activities, as its generation is not only traced back to mined metal(s) but also to the presence of sulfide minerals in the ore/rock being mined. For example, iron and base metals (e.g., Cu, Zn, and Pb) mining can contribute to AMD generation, but historically, coal mining has been the overwhelming contributor to AMD generation, especially from abandoned mines. Gold mining is also associated with ores that are particularly rich in pyrite, hence it can greatly contribute to AMD generation. As such, here, we focus on AMD derived from coal and gold mining activities. However, even from those two specific mining activities, AMD's concentration can greatly vary (**Table 1-5**).

2.1 Heavy metals concentrations

The primary pollutants in AMD are heavy metals, which are associated with high toxicity, non-biodegradability, and a tendency to bioaccumulate. Their concentrations in AMD are critical to assess both the environmental and human health risks. The often very high levels of Fe and, to a lesser extent, Al and Ni, along with smaller contributions of other heavy metals, reflect the hazardous nature of AMD (**Table 1**).

Table 1. Heavy metals range in coal and gold mine AMD.

Element	Concentration (mg/L)	Source	Reference
Al	10-545	Coal	[25], [26], [27].
	50-2830	Gold	
Fe	53.3-17640	Coal	[25], [28], [27].
	460-8600	Gold	
Mn	6.5-300	Coal	[29], [30]
	18-2575	Gold	
Zn	0.01-102	Coal	[31], [28], [32]
	0.01-55	Gold	
Cu	0.01-320	Coal	[28], [32], [33]
	0.01-65	Gold	
Cr	0.01-1.29	Coal	[27]
	3.2-20	Gold	
Pb	0.12-58.3	Coal	[28], [27]
	0.01-6.4	Gold	
Ni	1.1-922	Coal	[33], [34], [35].
	1.16-579	Gold	
Cd	0.001-1378	Coal	[36], [27].
	0.01-171	Gold	
Co	0.01-640	Coal	[37], [28, 35].
	0.01-41.3	Gold	

2.2 Alkali and alkaline-earth metals concentrations

Apart from heavy metals, alkali and alkaline-earth metals levels are also important, since these are components in neutralization and buffering reactions and therefore will dictate alkalinity and acidity concentrations. Alkali and alkaline-earth metals levels typically trace back to the source rock and can greatly vary. For example, gold AMD has significantly higher Mg concentrations and alkalinity compared to coal AMD (**Table 2**), as the source rock for gold is typically Mg and Ca-carbonate-rich (e.g., dolomite), therefore having higher neutralizing potential. Furthermore, post mining, the quality of AMD generated from underground or backfilled mines can be affected by the presence of sulfide or carbonate minerals that are further downstream. An overview of the composition of alkali and alkali-earth metals in coal and gold AMD is provided in **Table 2**.

Table 2. Composition of alkali and alkaline-earth metals, along with alkalinity and acidity, in coal and gold AMD.

Element	**Concentration (mg/L)**	**Source**	**Reference**
Na	0.01- 168	Coal	[37], [35]
	22-171	Gold	
K	0.01-28.3	Coal	[37], [38]
	1-18	Gold	
Ca	15.6-1070	Coal	[25], [29], [37]
	15-762	Gold	
Mg	7-474	Coal	[31]
	97-4564	Gold	
Alkalinity	0.06-14	Coal	[39], [38]
	16- 640	Gold	
Acidity	214-8133	Coal	[37]
	413-4200	Gold	

2.3 Sulfate, metalloids, and oxidation-reduction potential intensity

Water chemistry is also greatly affected by the key oxyanions (notably sulphates and to a lesser extent, nitrate, phosphate, and (bi)carbonate) contained in AMD, as well as less abundant metalloids, notably arsenic (As), boron (B), and silicon (Si). However, not only their concentration, but also AMD's oxidation-reduction potential (ORP) is important, as this defines their mobility. For example, the mobility of As heavily depends on pH and ORP. The release and transportation of these metalloids into the surrounding environment is harmful to human health and living organisms, even in low concentrations [40]. Typical composition of metalloids and oxyanions in coal and gold AMD, along with the ORP, are listed in **Table 3.**

Table 3. Composition of metalloids and oxyanions in coal and gold acid mine drainage.

Elements	Concentration (mg/L)	Source	Reference
As	0.02-32.2	Coal	[35], [27]
	0.02-1300	Gold	
B	0.01-1.1	Coal	[33], [41]
	0.01-5	Gold	
Si	0.01-30	Coal	[42], [43]
	0.01-1.49	Gold	
Sulphates	1950-30000	Coal	[25], [32]
	4000- 29547	Gold	
ORP (in mV)	119-568	Coal	[44], [27]
	10-657	Gold	

2.4 Rare earth elements concentrations

Depending on the geology of the area and mineral ore, AMD can also contain REEs [45, 46]. REEs are a group of seventeen (17) elements which include fifteen silvery white elements called lanthanides, ranging from lanthanum (La) to lutetium (Lu), along with scandium (Sc) and yttrium (Y). They are frequently classified into light REEs (LREE), which span from La to gadolinium (Gd), and heavy REEs (HREE), spanning from Terbium (Tb) to Lu, including Sc and Y [47]. REEs are typically encountered in very low concentrations in natural ores, making their extraction costly, with only a few commercial-viable deposits being currently exploited [48]. Considering that AMD contains relatively high concentrations of REEs, their recovery may be an alternative to their usual mining [20].

REEs can be found in AMD due to their leaching from the pyrite rock or nearby strata that contain them, ultimately migrating to AMD. Moreover, the migration and distribution of REEs in AMD has been reported to be driven by the presence of Fe, Al and Mn metals, as well as sulphates, while the hydro-chemical characteristics, such as pH, and transport mechanisms are also important [49, 50]. In turn, AMD treatment can concentrate the REEs content in the produced sludge, from which the REEs can be recovered and refined into marketable products [51]. **Table 4** illustrates the concentrations of REEs in coal and gold AMD.

Table 4. Concentrations of REEs found in coal and gold mine AMD.

Elements	Concentration (mg/L)	Source	Reference
Lanthanum (La)	0.005-845	Coal	[52], [53], [54]
	3.4-38.4	Gold	
Cerium (Ce)	0.01-5510	Coal	[52], [53], [32]
	8.1-210.4	Gold	
Praseodymium (Pr)	2.78-148	Coal	[37], [44], [55]
	0.9-56.7	Gold	
Neodymium (Nd)	0.001-310	Coal	[52], [53], [32], [55]
	3.7-222.5	Gold	
Samarium (Sm)	0.005-154	Coal	[52],[32], [44]
	1.1-72	Gold	
Europium (Eu)	0.87-37.1	Coal	[37], [44], [54], [55]
	0.3-10.2	Gold	
Gadolinium (Gd)	0.008-168	Coal	[32, 44]
	1.4-81	Gold	
Terbium (Tb)	0.70-28.5	Coal	[44], [55]
	0.2-7.1	Gold	
Dysprosium (Dy)	0.002-132	Coal	[32, 44]

	1.5-77	Gold	
Holmium (Ho)	0.87-35.5	Coal	[44], [53], [37]
	0.3-7.6	Gold	
Erbium (Er)	2.43-56.8	Coal	[44], [55]
	0.9-19.9	Gold	
Thulium (Tm)	0.34-12.3	Coal	[44], [37], [55]
	0.1-4.7	Gold	
Ytterbium (Yb)	1.99-51.2	Coal	[32], [44], [37]
	0.7-382	Gold	
Lutetium (Lu)	0.31-10.4	Coal	[44], [37], [55]
	0.1-4.0	Gold	
Scandium (Sc)	1.0-112	Coal	[52, 53]
	0.6-27	Gold	
Yttrium (Y)	0.11-2050	Coal	[53], [52]
	8.6-18	Gold	

2.5 Radionuclides concentrations

Another category of hazardous pollutants, which are naturally found in low concentrations in soil and water but can be released to the environment in high levels during mining activities, are radionuclides [56]. Specifically, radionuclides are usually an issue of concern during the mining of ores containing U [57]. However, they have also been found in low concentrations in gold and coal mines, ultimately leading to their release to the environment. As such, AMD can act as a carrier of these pollutants, ultimately transporting them to the different environmental compartments. On contact, and particularly when ingested by animals or humans, they cause exposure to severe ionising radiation, which damages the cells and tissues and even induces carcinogenic effects [58, 59]. The concentrations of radionuclides found in AMD from coal and gold mining activities are provided in **Table 5.**

Table 5. Concentrations of radionuclides found in AMD from gold and coal mining activities.

Elements	Concentration (mg/L)	Source	Reference
Uranium	0.2-785	Coal	[56], [55], [43]
	0.29-2668.9	Gold	
Thorium	0.1-11.9	Coal	[55], [56]
	0.7-80.7	Gold	
Radium	0.002-49.70	Coal	[60], [56]
	76-2811,9	Gold	
Radon	0.43-44.7	Coal	[61]
	32- 1060	Gold	

2.6 Paradigm shift in acid mine drainage treatment

AMD is notorious for its environmental repercussions owed to the elevated concentrations of toxic species, such as heavy metals, oxyanions, and radionuclides. It is also a significant issue in the mining industry, due to the treatment costs and secondary pollution it causes from the neutralisation processes, since this generates a hazardous sludge. However, recently, a paradigm shift, which is gaining momentum, has been observed, focusing on its sustainable management through valuable minerals recovery at affordable costs, such as REEs [47], introducing circularity, ZLD, and CLS opportunities. In a quest for prudent measures to avert challenges associated with AMD, numerous strategies and mechanisms for resource recovery have been explored. However, many challenges persist, such that some of the dissolved chemical species are found in very low concentrations, thus making their recoverability minimal and reducing their economic value. Nonetheless, there is also great potential for many others, whose recovery and reclamation will enable the reduction in the utilisation of virgin materials/resources, including freshwater, of which some are already scarce, and, instead, open avenues for the beneficiation and valorization of AMD [62], as discussed below.

3 Resource recovery

3.1 Recovery of metals

3.1.1 Recovery of main metals contained in acid mine drainage

AMD contains elevated concentrations of a variety of dissolved metals, with the dominant metals being Fe (and sulfur (S) as a non-metal), and to a smaller extent, Al and Mn, while other valuable metals, such as Cu, Pb, and Zn are also contained in its matrix [63]. As such, the recovery of these metals could provide a new revenue stream to support the treatment process, while their removal averts pollution issues and also creates water reclamation opportunities. This is the reason behind the recent paradigm shift from AMD prevention and conventional treatment [64] to resource recovery and valorization [63].

Fe recovery has long been examined [65]. For example, as early as the beginning of the 1990s, Rao, et al. (65) selectively recovered, at lab-scale, iron precipitates (ferric hydroxide, $Fe(OH)_3$) from AMD, by controlling its pH using lime, which were then used for ferric coagulant production. As research progressed, larger systems were explored. For example, Hu, et al. (64) used chemical oxidation (hydrogen peroxide, H_2O_2) coupled with selective precipitation (sodium hydroxide, NaOH) to recover Fe(III) from AMD in a pilot system, achieving 99.43% Fe removal and recovery. Akinwekomi, et al. (30) also selectively precipitated and recovered Fe from AMD in a pilot system by increasing the pH from ~2 to 4.5, using 10% sodium carbonate (Na_2CO_3) solution, thus demonstrating that no sophisticated technique is required to oxidise Fe(II) to Fe(III). Geochemical modelling and experimental results shed light on the fractional and step-wise recovery of Fe when using calcined cryptocrystalline magnesite nano-sheets [43], where Fe(II) was recovered at pH <3.5, while higher pH values led to the precipitation of other minerals, such as calcium sulphate (gypsum) ≥ 4-9, Al ≥ 4-6.5, Mn ≥ 8-

9.5, Cu ≥ 6-7, Zn ≥ 6-8, Pb ≥ 6.5-8, and Ni ≥ 9.5, yet sulphate precipitation under a broad range of pH was an issue, with Ca-free Mg or Na-based reagents greatly restricting this problem. However, other approaches to improve Fe purity have also been examined. For example, Flores, et al. (66) used calcium hydroxide ($Ca(OH)_2$) to increase the pH of AMD to 3.8 and selectively remove calcium sulphate and aluminium hydroxide, while NaOH was added to precipitate $Fe(OH)_2$ and slowly oxidise it, ultimately showing the viability of iron oxide recovery from AMD. Silva, et al. (67) explored the synthesis of magnetite particles using iron that was selectively precipitated at pH 3.6 from AMD. Specifically, ferric hydroxide precipitated and was subsequently separated using centrifugation and then dissolved in sulphuric acid (H_2SO_4) to produce ferric sulphate ($Fe_2(SO_4)_3$) and finally magnetite.

The selective recovery of Al, along with Fe, has also been examined. For example, Wei, et al. (34) used a two-stage precipitation ($Ca(OH)_2$) process to sequentially recover high purity Fe (>93.4% to >98.6% at pH 3.5 and 4.0, respectively) and Al (> 97.2% and >92.1% at pH 6.0 and 7.0, respectively) from AMD. Le, et al. (68) also selectively precipitated Fe (pH 3.0-4.0) and Al (pH 5.5-7.5) in a sequential fashion, and then a fluidized bed homogeneous crystallization system was used to recover Al(III), at pH 9.25, in crystalline pellets. High Fe(III) (99.7%) and Al(III) (99.3%) purities were obtained, while at high pH values, other metals, such as Mn, also co-precipitated.

In this regard, high levels of Mn can render AMD toxic, but also imply the potential for recovery. Silva, et al. (69) recovered Mn from mine water using sodium carbonate (Na_2CO_3), NaOH, or calcium carbonate ($CaCO_3$), to elevate the pH in the range 8.5 – 9.0 and remove over 99.8% of Mn from AMD. Yuan, et al. (70) used a less common approach, whereby chlorine salt (i.e., sodium chlorate ($NaClO_3$)) was used to oxidise and subsequently recover Mn from a manganese ore leaching mixture, which is chemically similar to AMD, and recovered 90% of Mn, along with Zn and Cu that were present in the solution.

Other metals have also been successfully recovered from AMD. For example, MacIngova and Luptakova (71) explored the recovery efficacy of Fe, Al, Cu, Mn, and Zn from AMD through sequential selective precipitation, while Sahinkaya, et al. (72) used sulfide to precipitate Cu and Zn from AMD in an anaerobic baffled reactor, where Cu was recovered at >84% under pH of 2, while Zn was recovered at 84 – 98% at neutral pH (7.0 - 7.5). Pino, et al. (73) recovered high purity (97%) Cu from AMD using nanofiltration, while Oh, et al. (74) selectively precipitated Cu and Zn (90% precipitation rate) from AMD at pilot scale and in an active mine, achieving high (80%) purities. Furthermore, Tabak, et al. (75) used selective, sequential precipitation to remove metals and sulfides from AMD, where 99.8% of Al, 99.7% of Cd, 99.1% of Co, 99.8% of Cu, 97.1% of Mn, 47.8% of Ni, and 100% of Zn were removed and recovered using hydrogen sulfide (H_2S) in a sequencing batch reactor, ultimately reclaiming water that mainly contained benign ions, such as Ca and Mg, and allowable concentrations of sulphate and sulfide for potable water use.

3.1.2 Recovery of rare earth elements

REEs can also be found in AMD, but at relatively low concentrations. Yet, their importance in the high-tech industry, among others, has made their recovery from AMD imperative due to increasing demand [47]. For the recovery of REEs from AMD, different technologies, such as chemical precipitation, solvent extraction, ion flotation, ion exchange, and adsorption, have been examined, as summarised below.

3.1.2.1 Chemical precipitation

Chemical precipitation is one of the most frequently used methods for resource recovery from AMD, including REEs, due to its relatively simple operation, low capital investment, and its ability to precipitate a wide array of metals [47]. This technique involves the use of an alkaline agent, such as lime, to increase the pH of AMD, thus enabling metals to precipitate as hydroxides or oxides, along with the removal of sulphates and carbonates. Precipitation is underpinned by mechanisms, such as neutralisation, complexation, co-precipitation, reduction-oxidation (REDOX), adsorption and co-adsorption, which effectively facilitate the recovery of valuable minerals from the matrices of AMD. However, chemical precipitation involves numerous steps in the wastewater treatment process and is typically characterised by high costs for equipment maintenance [76].

For REE precipitation from AMD, H_2O_2 can facilitate, at pH > 6, the conversion of Fe(II) to Fe(III) and its precipitation, while higher pH values can significantly increase REEs precipitation due to the elimination of Fe-Al competitive adsorption [77]. In general, conventional AMD treatment techniques typically involve the use of chemicals that contain hydroxides (OH) to neutralize the solution, thereby leading to approximately 70% of REEs to precipitate out at the desired pH level, while the remaining 30% is released with the treated effluent [78]. To improve REEs recovery efficiency, Hassas, et al. (78) applied a unique and effective tiered precipitation method using NaOH and CO_2 mineralization, and achieved >85% recovery efficiency for pH values >7, whilst repressing the majority of the Fe content precipitation.

REEs can be recovered from AMD through phosphate precipitation, due to the strong affinity between phosphate conjugate and the lanthanides and yttrium, as compared to sulphate. For example, Chávez used a two-step process, where Fe and Al were first selectively removed via hydroxide precipitation, and then phosphate was added for REEs precipitation (90±5% recovery) [79]. Potassium hydroxide (KOH) has also been examined for AMD neutralisation, where co-precipitation with REEs takes place. For example, Moraes et al [80] reported the precipitation of amorphous sludge that contained a high (14%) REEs concentration, which, through sequential extraction using acetic acid, was able to leach 60% from the precipitate, revealing AMD potential as a secondary source for REEs. NaOH can also be used for REEs recovery. For example, Vaziri Hassas, et al. (81) used CO_2 mineralization and NaOH neutralization to recover Al (≥90%) and REEs (≥85%) from AMD at low (<7) pH when using phosphate or carbonate as ligands. Finally, Goodman, et al. (55) used a strong hydroxide base (NaOH or KOH) in a two-step process to control the pH to 4.0 and remove Fe and thorium, which can interfere with REEs recovery, and then the pH was increased to 7.5 to precipitate Al-REEs complexes, achieving a 90% REEs removal.

3.1.2.2 Adsorption

Adsorption has also been examined for REEs recovery from AMD [82]. It is a surface phenomenon where a solid substance (adsorbent) selectively removes dissolved species (adsorbate) from the aqueous solution and therefore can be used for the adhesion (electrostatic forces) of dissolved metal(s) onto the surfaces of solid materials [20]. It is widely applied due to its relative ease of scalability and operation, low cost, high removal efficiency and ability to accommodate a variety of adsorbents [83].

Different adsorbents have been examined for REEs recovery from AMD. Wang, et al [76] chemically anchored pyrrolidine diglycolamide (PDGA) into silica and the functionalised PDGA-silica material recovered, under optimal working conditions, 78.4% La, 85.1% Nd, 75.7% Gd, and 82.3% erbium (Er). Callura, et al [84] improved by 137-fold REE selectivity of aminated resins through functionalisation using N,N-bis(phosponomethyl)glycine (BPG), which resulted in a 236 concentration factor compared to AMD. Following recovery, purity was enhanced by more than ten-fold, which indicates that high purity REEs can be recovered from low-concentration sources like AMD. N- and O-ligand silica-chitosan hybrid beads also have great potential, considering that within 5 minutes of contact time, these beads demonstrated adsorption and >90% REE recovery, while (1-(2-pyridylazo) 2-naphthol (PAN) gels exhibited higher efficiency than acetylacetone silica gels [85].

Overall, REEs recovery from AMD through adsorption appears promising due to low costs, ease of operation, high scalability, economic viability, and reusability (or regeneration) of the adsorbent material [86, 87]. Yet, many challenges persist, mainly regarding REEs selectivity due to the complex nature of the AMD that contains elevated concentrations of competing ions [88]. Furthermore, REEs tend to have similar properties to each other, thus making it difficult to achieve high-purity individual REE recovery [89].

3.1.2.3 Solvent extraction

In solvent extraction (or liquid-liquid extraction (LLE)), REE-containing AMD is vigorously mixed with an immiscible organic phase (extractant) to selectively remove REEs from AMD to the organic phase, while most other metal ions will remain in the raffinate (REE-lean AMD) [90]. Solvent extraction has been the most popular approach for REEs recovery at an industrial scale in recent years, due to its high efficiency, ability to handle large volumes, and ease of operation [21]. However, it can be costly to operate as extractants tend to be expensive [91]. Different studies have examined different solvent extractants for REE recovery from AMD. For example, Abreu and Morais (92) evaluated different extractants (DEHPA, IONQUEST® 801, Cyanex 272, TOPS 99, and EHEHPA), where DEHPA and IONQUEST® 801 displayed the best overall efficiency in REE recovery from AMD, with the latter exhibiting higher separation factors between adjacent REEs. The use of ionic liquids, instead of commercial extractants, has also been identified as a viable option for REE large-scale extraction from sulphate-rich AMD due to excellent loading and high separation factors and extraction efficiencies [22].

The main advantage of solvent extraction is its selectivity in extracting REEs through distinctly separating the elements as individuals or groups (i.e., heavy REEs or light REEs) [93]. However, it also requires high capital expenditures (CapEx) and operational expenditures (OpEx) to operate, as sophisticated equipment and large amounts of expensive organic solvents are required [47]. Finally, after solvent extraction, the organic solvents need to be treated before disposal, as these tend to be highly flammable and toxic, thereby adding to process cost [94].

3.1.2.4 Ion exchange

Ion exchange (IX) employs functionalized polymers to treat wastewater [95], targeting the removal of specific ions [94]. Its operation greatly depends on the local characteristics of AMD, and it can be efficient, versatile, and selective in recovering REEs from secondary sources [96]. However, it is also expensive to operate, has limited capacity, and can potentially lead to the generation of toxic wastes/by-products [97]. Experimental and theoretical (mechanistic) methods have been employed to study the IX reactions when recovering REEs from AMD.

For example, Silva, et al. [98] used cationic resins to recover REEs through IX and discovered that best elution occurs in calcium chloride ($CaCl_2$) solution, with batch loading results showing strongly acidic cation resin can successfully uptake over 95 % of La and Y from AMD, while continuous elution studies reveal that 2.0 mol/L calcium chloride elutes 100 % La and 85 % Y from the resin. Felipe, et al. (99) also examined a cationic resin for REEs recovery from AMD. Results demonstrated higher selectivity for light REEs than heavy REEs, while REE recovery was more efficient at acidic conditions (pH 1.4-3.4), while the sorption patterns of REEs in two commercial cationic resins, i.e., Dowex 50WX8 and LEWATIT® MDS 200 H, showed great promise. José and Ladeira (100) obtained similar results, since the LEWATIT® MDS 200 H resin demonstrated a high selectivity for REEs, particularly for light REEs, and a low affinity for impurities (Ca, Al, and Mg), while REEs removal efficiency from AMD was 83%, and a loading efficiency of 85% was obtained at an REE loading capacity of 0.940 mmol/g. Felipe, et al. (101) also deduced that cationic exchange resins were more favourable for light REEs than heavy REEs recovery from AMD when the pH was in the range of 1.4 - 3.4. Finally, Hermassi, et al. (102), employed precipitation, IX, and selective separation to recover REEs from AMD that contained approximately 0.25g REE/L (concentrated REE sulphuric solution), where Xenotime (YPO_4(s)) and Cheralite ($CePO_4$(s)) were the major recovered minerals.

An overview of the different techniques for REEs recovery from AMD, along with their main advantages and disadvantages, is shown in **Table 6.**

Table 6. Comparison of different techniques for REEs recovery from AMD**.**

Technology	Maturity	Costs	Advantages	Shortfalls	References
Chemical precipitation	High	Low-Medium	Reasonable cost for initial operation. Ease of operation.	Large volumes of secondary sludge require proper handling and further treatment. Co-precipitation of impurities.	[87, 103]
Adsorption	Low	Low	Regeneration ability. Low cost. Ease of operation.	Generation of secondary pollution. Low selectivity.	[88, 89]
Solvent extraction	Intermediate	High	High purity of recovered products. High selectivity.	Organic solvents are expensive. Repetitive extractions to acquire high purity. Uses flammable organic solvents.	[18, 104, 105]

Ion exchange	Intermediate	High	High recovery rate. High selectivity.	Susceptible to fouling. High cost of resins.	[106, 107]

3.2 Sulphate recovery

Apart from iron, sulphate is another chemical species that is abundant in AMD, particularly when FeS_2 is oxidised in coal seams or strata, thus suggesting the great potential for its recovery. Numerous studies have explored the recovery of sulphate from AMD through precipitation. For example, Akinwekomi, et al. (30) recovered sulphate from AMD as gypsum through lime dosing. Other studies have demonstrated that de-silicated fly ash (DFA) can recover sulphate from AMD through adsorption, with over 50% recovery, while at an elevated temperature of 35 °C and an extended contact time of 90 minutes, 75% of sulphate was recovered from AMD [108]. Sulphate removal from AMD via ettringite precipitation has also been studied, where more than 99% removal has been achieved [109].

In addition, membrane filtration has also been explored for sulphate recovery from AMD, along with water reclamation [110]. For example, PreuB, et al. (111) employed nanofiltration to remove sulphate from AMD, achieving 96% removal efficiency (from an initial 1850 ppm to 65 ppm after the recovery process). Martí-Calatayud, et al. (112) employed a three-compartment electrodialysis (ED) system to recover H_2SO_4 from the sulphate content in AMD, with current efficiency being stable over time, ensuring sufficient recovery rates, while the optimal current density was 2.5 mA/cm^2, after which recovery rates began to decrease. Finally, Kesieme, et al. (113) assessed the feasibility of H_2SO_4 recovery from AMD through direct contact membrane distillation (DCMD), achieving over 99.9% recovery at 60 °C and 20-31 $kg/m^2/h$ flux.

3.3 Water reclamation

Pollution and water scarcity have necessitated the reclamation and reuse of water to supplement the dwindling freshwater resources. AMD presents a certain challenge, although vast amounts of polluted water are encountered in this form, with 360 ML being generated daily in South Africa alone, a water-scarce country [114], water is not readily usable. As such, research has focused on water reclamation from AMD, for different uses, such as domestic, irrigation, and industrial purposes, often aiming at creating a ZLD system [63] using different technologies, such as reverse osmosis [30].

For example, Pino, et al. (73) used nanofiltration, at pilot-scale, and were able to reclaim 80% of the water that was initially contained in AMD. Aguiar, et al. (115) used a single nanofiltration (NF270 membrane) step for water reclamation from gold AMD and the maximum water recovery rate was 60%, with a sharp decline in conductivity retention efficiency having been observed thereafter. Wang, et al. (116) used DCMD and reclaimed 60% of water from pre-treated AMD, observing just a 22% flux decrease. Masindi, et al. (117) used a combination of magnesite, lime, and CO_2 bubbling for minerals recovery and water reclamation from AMD, while when reverse osmosis was added to this process, drinking water could be reclaimed [28]. Buzzi, et al. (118) used electrodialysis to reclaim water from coal AMD, reaching very high (≥97%) removals for the main contaminants found in AMD; however, scaling was an issue.

Overall, water reclamation from AMD is feasible, even at industrial scales, with the intended use of the reclaimed water (e.g., irrigation or potable water) defining the treatment technology(ies) that will be used. Often membrane processes [119, 120] are employed, such as reverse osmosis which has shown potential even for drinking water reclamation from AMD [121]. In these cases, a concentrated brine is also produced, but when viewed under the resource recovery paradigm, this can be an important by-product rather than a waste. However, given that AMD contains very high dissolved ions (salts) concentrations, membrane scaling, high cost and energy demand, and low water permeability can affect the process [74].

Therefore, the long-term stability of the reclaimed water quality (e.g., membrane integrity) necessitates continuous monitoring [122]. Not only this, but reclaimed water needs to be constantly monitored, given that AMD contains toxic chemical species, such as heavy metals, which should not be benchmarked alone, but toxicity-based methods that consider the overall biological effect ("masked" toxicity) should be employed [123].

3.4 Factors affecting metals and minerals recovery from acid mine drainage

Despite the many benefits, resource recovery from AMD is also associated with many challenges, with one of the most notable ones being impurities from co-precipitation. In most cases, Fe (and sulphate) tends to co-precipitate with other metals, ultimately affecting the purity and quality of the product material. This is even the case for ores, such as bastnaesite, where REEs recovery from the bastnaesite pre-concentrate was contaminated by impurities, such as Fe, Al, Mg and Th [124]. Another factor affecting metals and minerals recovery from AMD can be their very low concentrations, particularly for REEs [96].

Chemical affinity can also affect the recovery process, as certain ions and molecules tend to participate in chemical reactions and form stable complexes, while sulphate can also act as a ligand [125]. This refers to how different metal ions interact with other elements in the solution, like hydroxides, sulphates, and other anions that are encountered in AMD [126]. Chemical affinity is an important notion since it determines the possibility and intensity of these interactions, which affects how well metal recovery methods work. According to Rodriguez, et al. (127), the presence of various metal ions in AMD reduces the viability of selective recovery due to chemical affinity since similar complexes are usually formed with accessible ligands. For instance, Fe and Al usually form hydroxides when hydroxide ions (OH^-) are available in the aqueous stream [128]. This phenomenon is also caused by the similar pH conditions of the two metals, which make them compete for the anions; hence, selective precipitation is a challenge when only single metals are targeted [129]. As a result, highly specific ligands or advanced separation methods have been explored, where specific compounds have been synthesized to attach to a specific metal, such that co-precipitation is avoided. Chelating compounds, such as ethylenediaminetetraacetic acid (EDTA), can form potent complexes with particular metals; nevertheless, their use needs to be precisely calibrated to prioritize the target metal over other metals [130].

Physical separation methods, such as solvent extraction, membrane filtration, and ion exchange, are used to improve selectivity, in addition to chemical specificity. For example, ion exchange resins can be modified to selectively bind with specific metal ions, based on charge, size, and coordination environment. Solvent extraction is another method for selectively recovering metals, as certain metal complexes are selectively dissolved by organic solvents, enabling the metals to be separated from the aqueous phase [131].

Ionic strength is another factor that hinders metal recovery from AMD. The overall concentration of ions in a solution is indicated by its ionic strength. The ionic strength can be very high in AMD, as it usually contains large quantities of anions like SO_4^{2-} and different metal cations such as Fe^{3+}, Al^{3+}, Mn^{2+}, Cu^{2+}, and Zn^{2+} [132, 133]. Due to its high ionic strength, ions in AMD behave differently due to altered activity coefficients. As such, an adjustment for the non-ideal behaviour of ions in concentrated solutions is provided by the activity coefficient. The activity coefficients of the ions decrease with increasing ionic strength, hence decreasing their chemical activity and impacting solubility and precipitation reactions [134]. The common ion effect, which refers to the decrease in the solubility of an ionic compound when a common ion is added to the solution, is also particularly relevant in AMD, where high concentrations of sulphates and other ions are present [135]. For example, high SO_4^{2-} concentration in AMD can trigger the natural precipitation of metals as metal sulfates, e.g., Zn as zinc sulphate ($ZnSO_4$).

Furthermore, stable complexes with SO_4^{2-} (e.g. gypsum) are formed during metals/minerals precipitation, which can prevent the removal of other metals (e.g., Zn and Cu) from the AMD, thus complicating the recovery process as SO_4^{2-} has reduced availability in the reaction. Furthermore, these competing ions can shift reactions to equilibrium, further reducing the efficiency of metal recovery processes [136]. The solubility of metal ions in AMD is also influenced by the ionic strength and the presence of complexing agents. The formation of ionic pairs and complexes causes the solubility of metal ions to decrease when the ionic strength increases [137, 138].

Finally, during metals/minerals recovery from AMD, these usually bind to ligands to establish stable compounds [139], ultimately affecting the solubility, mobility, and reactivity of metal ions. Furthermore, research has reported that when SO_4^{2-} ions are dominant in the AMD, they can form complexes with a variety of heavy metals as well as with REEs [140]. For example, REEs can form soluble REE-sulphate complexes, as illustrated in **Equation 1**.

$$\mathrm{REE}^{3+} + SO_4^{2-} \rightarrow \mathrm{REE(SO)}_4^{+} \qquad (1)$$

The direct precipitation of REEs may be hampered by these complexes, since they are frequently more soluble in water than their un-complexed counterparts. For traditional precipitation techniques that depend on the formation of insoluble compounds to separate and recover metals, this enhanced solubility presents a serious obstacle [141].

4 Industrial pathways for the recovered metals and minerals

4.1 Industrial iron-based products

4.1.1 Coagulants

Historically, coagulants have been used for (waste)water treatment, primarily for the removal of suspended solids, with Al and Fe being the most common constituents of inorganic coagulants. AMD is particularly rich in Fe, and it often contains high Al levels; therefore, even raw AMD has been explored as a coagulant for (waste)water treatment. For example, Lopes, et al. (142) used 15 mL of AMD to treat 1 L of sewage, where 74% of suspended solids, 62% of COD, 65% of BOD_5, and 97% of phosphorus were removed, while when Fenton's Reaction was also used, percentage removals increased to 78% for suspended solids, 80% for COD, 80% for BOD_5, and 98% for phosphorus. Aslam, et al. (143) explored the treatment of municipal wastewater using raw AMD, where the results showed high efficiency when compared to AMD-recovered Fe-rich catalysts, i.e., magnetite, hematite, and goethite. Huang, et al. (144) also used AMD to remove ciprofloxacin (CIP), a broad-spectrum fluoroquinolone antibiotic, and 89% of CIP removal was observed after 60 minutes contact time, thus showing opportunities of leveraging the Fe and Al content in AMD for contaminants removal (coagulation but also adsorption) from water. However, apart from Fe and Al, raw AMD contains a wide array of contaminants in its matrix, including heavy metals, and this suggest its limited practical potential as a coagulant. For this reason, focus has been placed on the selective recovery of Fe (and Al) from AMD and used for coagulant synthesis.

For instance, Menezes, et al. (145) synthesized poly-alumino-iron sulphate (PAFS) coagulant from AMD by first oxidising Fe(II) into Fe(III) (at pH 2.5- 3.0 for 24 hours), using potassium dichromate to monitor Fe(II) oxidation, and then dissolve the recovered precipitate in H_2SO_4 to synthesize the sulfate-based coagulant, which contained 72% ferric iron and 27.5% aluminium that was recovered from AMD. Similarly, Mwewa, et al. (146) synthesized PAFS, by increasing AMD's pH to 5.0 and precipitating 99.9% Fe and 94.7% Al content. Then, the precipitates were dissolved in H_2SO_4 to synthesize the PAFS coagulant, which was found as effective as conventional coagulants in COD (56.0%) and turbidity (91.9%) removal from brewery wastewater.

Fe-based salts, such as ferric chloride ($FeCl_3$) and ferric sulphate ($Fe_2(SO_4)_3$), are widely used coagulants, as they are effective in lowering turbidity, removing color, and precipitating metals and other pollutants from (waste)water while they can be easily synthesized by simply reacting Fe(III) and H_2SO_4 [147]. This approach has been replicated in both uses of Fe-rich mine tailings and AMD. For example, Almeida and Schneider (148) leached iron ore tailings with HCl at 80 °C for 120 min and recovered 94% Fe from the tailings, producing $FeCl_3$ as a coagulant, which was able to remove ≥98% turbidity from raw water. Another study tested the efficacy of a P-doped poly-ferric chloride coagulant synthesized from pickling sludge through oxidation of Fe by $\mathrm{H_2O_2}$, followed by preparation of the coagulant using disodium phosphate ($\mathrm{Na_2HPO_4}$), removing 96.25% of color and 69.91% of the COD from dyeing wastewater [149].

4.1.2 Adsorbents

Fe-based adsorbents, such as magnetite, are widely used in the water and wastewater industry as well as in emerging applications in contaminants removal due to their high adsorption capacities [150], minimal toxicity, low cost, and high availability. Their efficiency lies in their high surface area, high porosity, and strong magnetic properties, which contribute to their ability to efficiently remove contaminants from water [151, 152]. For example, Fe (as well as Al and Zn) (hydr)oxides, which can easily be recovered from AMD, can effectively adsorb phosphate from wastewater matrices, thereby mitigating eutrophication [153]. Such adsorbents can also have industrial applications, highlighting that the waste (AMD) of one industrial process (mining industry) can be valorised in another industrial process (wastewater adsorption). For example, Muedi, et al. (154) synthesized Fe/Al di-metal nanostructured composite (adsorption capacity 411 mg·g^{-1}) from Fe(III) and Al(III) recovered from real coal AMD and used it to remove Congo red dye from water, achieving ≥99% removal and highlighting possible industrial applications (e.g., for tannery wastewater treatment). Furthermore, research has also proven that toxic pollutants, such as arsenic, chromium, phosphate, chloro-organics, and waterborne bacteria (e.g., *E. coli*), can also be removed from (waste)water through adsorption techniques involving the use of Fe-based adsorbents [155]. For example, Akinwekomi, et al. (30) used selective and fractional precipitation to recover high purity (>99%) hematite from coal AMD, which is a well-known industrial adsorbent that can effectively remove toxic contaminants from water such as phosphate and arsenic.

4.1.3 Pigments

Amongst other important Fe-based minerals that can be recovered from AMD are pigments [156]. Pigments can be synthesized from AMD through the recovery of Fe as iron oxides, and this not only helps reduce the ecological footprint of AMD, but it can also foster the introduction of circular economy in its management [30, 157]. In this regard, Ryan, et al. (158) recovered iron oxides from AMD through selective precipitation, where Fe(III) was precipitated at a pH of 3, thus ensuring that other metals like Al and Mn remained dissolved, resulting in a high purity material with intense yellow color, which suggests the recovery of goethite, an industrial marketable synthetic iron oxide pigment. Also, magnetite, an important mineral with wide industrial applications, and a crucial pigment, has been effectively recovered from AMD in high purity [63, 67, 159]. Finally, Tabak, et al. (75) recovered metal precipitates and minerals from AMD and then transformed them into valuable pigments that can be commercially viable as they met industrial standards for color intensity, stability, and purity.

4.1.4 Catalysts

Fe-based catalysts are widely employed across many industries and are important in environmental applications, as they are associated with low costs and toxicity and have different oxidation states. Lappas, et al. (160) shown that it is technologically feasible and potentially economically viable to recover Fe from AMD, while notable Fe-based catalysts include goethite and particularly magnetite, which can be effectively recovered from AMD at high-purities [66]. Different recovery techniques have been explored, while catalysts have been used for different applications, such as advanced wastewater treatment. For instance, Sun, et al. (161) used a novel air-cathode fuel cell to treat AMD and recovered iron, which was then used to produce three electro-Fenton catalysts, namely goethite/graphite, hematite/graphite, and magnetite/graphite, which when used in advanced wastewater treatment (Rhodamine B (Rh B) removal) and found promising, particularly the Hematite/Graphite (95.4% Rh B removal) and Magnetite/Graphite (95.6% Rh B removal). In another study by Sun, et al. (162), iron oxide/carbon composite was modified through electron-Fenton catalyst using Fe(II) recovered from AMD by applying air-cathode fuel cell (AC-FC) method, while the treated AMD met the requirements of the prescribed discharge standards. Aslam, et al. (143) also produced a Fe-based catalyst using magnetite, hematite, and goethite recovered from Fe-rich AMD and used it for municipal wastewater treatment through the solar photo-Fenton process. Results showed that 99% of COD removal was achieved at pH 2.8, thus underscoring the efficacy of the Fe-based catalysts synthesized from AMD for COD removal.

Other possible applications of the recovered Fe can be its use as fused iron catalysts, as these are also widely used in low- and high-temperature Fischer-Tropsch processes, mainly to convert synthetic gas (syngas) into hydrocarbons [160, 163]. The increasing industrial interest in developing optimized iron catalysts for the Fischer-Tropsch processes is also reflected in the Bromfield and Vosloo (164) study, where a new Fe-based catalyst was synthesized for the high-temperature Fischer-Tropsch process. Finally, Lefèvre and Dodelet (165) conducted a study which examined the reduction of oxygen in a polymer electrolyte membrane fuel cell by using Fe-based catalysts, revealing the many possibilities of using AMD as a secondary source of metals and notably Fe.

4.2 Industrial uses of other recovered metals and minerals

Apart from Fe, other metals, such as Al, Mn, Cu and Zn, which are typically encountered in AMD [166], can be selectively recovered and used for different industrial applications. For example, Al, which usually co-exists with Fe, can be recovered from AMD as (hydr)oxides [156]. Such materials have the potential to be used in different industrial applications. For instance, Muedi, et al. (167) recovered and valorised Al, along with Fe, from coal AMD, and used it for nutrients removal from municipal wastewater, achieving >96% removal. Mn is another important metal that can be recovered and valorized from AMD, typically as (hydr)oxide. Industrial applications include their use as additives in the manufacturing process of steel, cement, and other construction materials to improve mechanical strength [168]. Manganese oxides are also crucial as catalysts and electrode materials in many battery types [169]. As mentioned above, the production of pigments from AMD has been widely studied and explored, where, apart from Fe, Al and Mn have also been transformed into pigments (usually containing Fe) that can be beneficial in the paint industry [170]. On the other hand, Zn and Cu, which can be recovered in relatively high purities from AMD, can be used in the production of electrical and electronic components, including batteries, electrical connectors and other electronic components, and manufacturing of brass alloys [171, 172]. As such, the recovery of additional metals and minerals from AMD, apart from Fe, can further underpin the waste-to-resource paradigm.

4.3 Recovery of rare earth elements and their industrial applications

REE mining is challenging and also notorious for its environmental impact [20]. Yet, REEs are important in many industrial applications, underpinning the growing interest in creating national reserves, which has stimulated interest in REEs secondary sources such as AMD [173].

In this regard, Song, et al. (21) highlighted that AMD can be an alternative REEs source, especially for Ce, La and Nd, which are in high industrial demand. The recovered REEs from AMD (green mining) can be used for the production of fluorescent lighting, batteries, computers, and cell phones [174], along with their use in power generation and energy efficiency due to their unique magnetic, luminescent, and chemical properties [175]. For example, Tb, Eu, and Yb phosphors can be used in fluorescent light bulbs and older generation light-emitting diodes (LEDs), La in camera lenses, while Y, Ce, La, Eu, and Tb can be used in cathode ray tubes and flat panel displays [176, 177].

Other industrial applications extend to the production of REE-enriched catalysts, which can crack (break down) heavy hydrocarbon molecules into smaller ones, thus allowing petroleum refineries to produce more product per barrel of oil processed [178]. In autocatalytic converters, Ce can provide an oxygen-rich atmosphere that aids in the oxidation of hazardous carbon monoxide into carbon dioxide [179], while Nd, Pr and Y are also employed as catalysts in autocatalytic converters to further restrict carbon monoxide emissions. It is also possible to recover cerium oxide from AMD, which is commonly employed in the manufacture of glass types that require precision polishing, including flat panel display screens and/or to lighten glass [173].

Furthermore, permanent magnet manufacturing require Pr, Sm, Nd, Tb, and Dy, which are crucial in wind turbines and electric vehicle (EV) motors, highlighting REEs importance in renewable energy generation [180]. The importance of such an application is reflected in the fact that, according to IEA (181), clean energy technologies, which are in high demand, account for 91% of the entire value of the worldwide REEs metal market. Furthermore, Y is a basic component of superconducting electric power lines, and this can be separated from other recovered REEs through solvent extraction [182, 183]. Sc is a promising material for new generation thin-film voltaics due to its photovoltaic characteristics, particularly in compounds with Cu, In, and Ga [184]. The different industrial applications of typical REEs, along with the current and future demand market share of these elements, are illustrated in **Figure 1**.

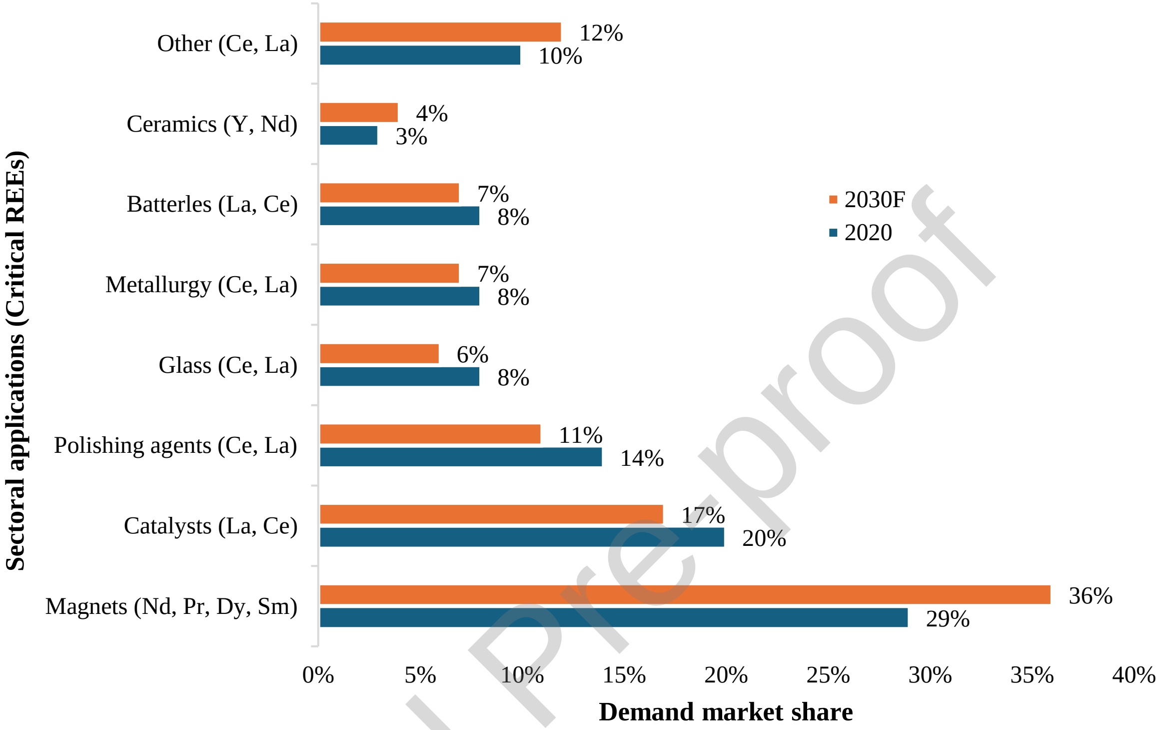

Figure 1: Applications of different rare earth metals across various sectors in 2020 and in 2030 (forecast) [185].

Specifically, the current rapid growth in the REEs market traces back to green energy and EV motors [186]. Additionally, the growing demand for electronics, such as smartphones, tablets and laptops, has caused an unprecedented market expansion of REEs, particularly for Pr and Dy [187]. On the other hand, Ce and La are the most used REEs [188, 189], but their applications have been observed to be slightly limited, as compared to other rare earths, which are found in lower concentrations in the Earth's crust. As a result, the demand for other REEs, particularly Nd, is increasing despite its relative scarcity, mainly due to its use in permanent magnets [90].

5 Economic viability and market analysis

5.1 Offsetting acid mine drainage treatment cost through resource recovery

Conventional AMD treatment (e.g., neutralization) can be costly, while it also produces secondary waste streams, such as sludge, that require further disposal and remediation [151]. The management of this secondary sludge has been identified as a significant challenge and can greatly increase treatment costs [190]. More robust treatment methods, such as membrane technologies, apart from generating concentrated brines that are difficult to manage, are also expensive to install and operate. For instance, in a case study dealing with gold AMD treatment, the capital cost of an employed ultrafiltration-nanofiltration unit with a volumetric flow rate of 15 m^3/h was USD$131250, while the operational cost was 0.263 USD$/$m^3$ [115].

According to the Fortune Business Insights (191), the global market share for AMD treatment was 23.71% of the total mining waste management in 2020, amounting to USD$1136.6 million. For this reason, research has focused on reducing waste sludge generation through the recovery of valuable products that have different industrial uses, such as water treatment, soil remediation, agriculture, and construction [192]. This can provide new revenue streams that can offset treatment costs or make the process even self-sustainable. For example, Hu, et al. (64) recovered Fe from AMD, using H_2O_2 and NaOH a pilot scale (12 m^3/d), and the process was more cost-effective than conventional neutralization with lime, saving USD$0.14 per m^3 AMD. The authors further noted that when considering a USD$43.05 treatment cost per ton of AMD sludge, then an additional USD$2.91 million will be avoided from an existing AMD treatment plant (33,000 m^3/d), which annually produces about 300,000 tons of refractory sludge. Le, et al. (68) used sequential selective precipitation and fluidized bed homogeneous crystallization to recover Fe and Al from AMD, and the process was self-sustainable, as the avoided wastewater treatment cost (USD$2.05 per m^3) along with the revenue from the iron product (USD$1410/ton) and the aluminium pellets (USD$1089/ton) could provide an estimated profit of USD$1.31/m^3-AMD treated.

Apart from Fe and Al, other by-products, such as H_2SO_4, can be produced from AMD [193], and can also reduce the operational costs [114]. However, REEs have gathered the majority of attention, as these are typically high-value by-products. In a case study, AMD was pre-concentrated using a two-step precipitation (neutralization) process, which typically produces a REE-rich (1% to 5%) sludge with low (up to 15%) moisture content which has been estimated to hold a market value of USD$60.76/kg [22]. However, the commercial viability of such initiatives is influenced by the cumulative cost of the extraction, purification and refining processes, as well as the market price of the targeted REEs [194].

To make AMD-derived REEs price competitive, research has focused on optimising the recovery processes and reducing its cost. Recovery of REEs from complex streams, such as AMD, has become more practical and cost-effective owing to developments in separation and extraction technologies [47, 195]. Many different estimates for the REEs market size exist, which can greatly vary. Nonetheless, all agree that the unique properties of REEs will drive a strong compound annual growth rate (CAGR) in the years to come, with some estimating a three-fold increase in their market size between 2022 (around USD$5 billion) to 2033 (USD$14.6 billion) [196], as shown in **Figure 2**.

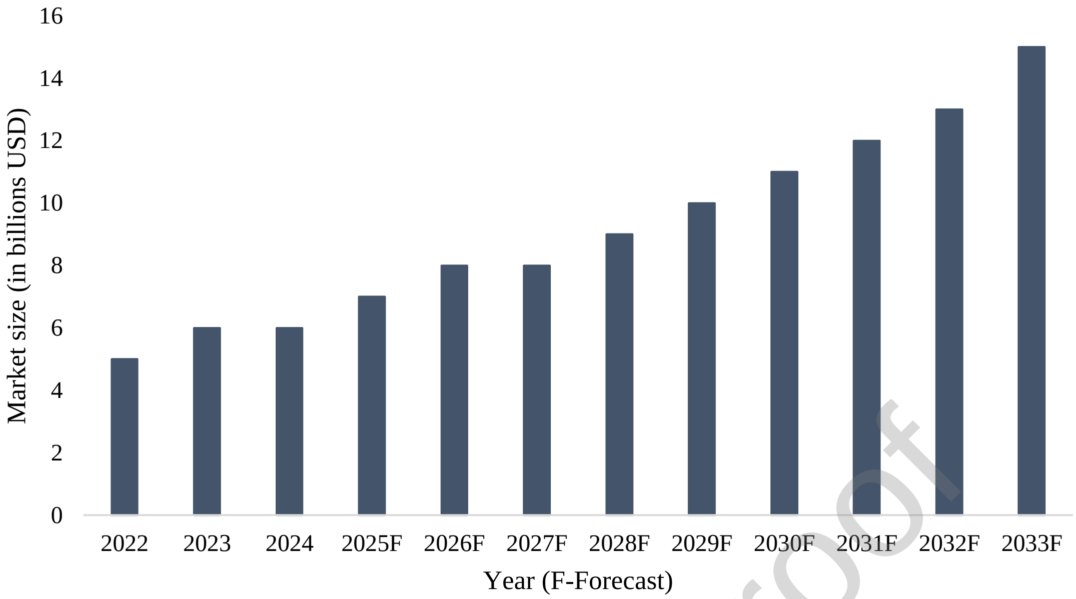

Figure 2: Global market size for rare earth metals between 2022 to 2033 (forecast) [196].

5.2 Market share for the main rare earth elements contained in acid mine drainage

In general, REEs-rich AMD typically contains elevated concentrations of La, Ce, Nd, Gd, Y and Dy as compared to the rest of the REEs Felipe, et al. (99). For this reason, here, each of these elements is separately discussed in terms of its market share. We note that the given values are only estimates for their global market and therefore future projections could be associated with high levels of uncertainty.

5.2.1 Lanthanum

La is a silvery-white metal that is soft, malleable, and ductile [197], while is the second most abundant rare earth metal after Ce [198]. It is the most reactive rare earth metal after Eu and oxidises to form La_2O_3 in the presence of oxygen (i.e., air) at ambient temperature [199]. This metal is commonly utilized to manufacture carbon arc lights for use in cinematography, studio lighting, and projector lights and is also found (>25%) in mischmetal used to manufacture lighter flints [200]. La is also used in a variety of automotive and aerospace applications, which has led to a considerable increase in its market globally [201]. Various industries, including consumer electronics and hybrid electric cars, have a great need for La as a result of the substantial rarity of rare earth metals in developing regions such as Asia Pacific [173].

In the coming years, the demand for La is anticipated to be driven by a variety of factors, including the development of electronics, electric cars, and the automotive sector. The market has expanded, in part because of the increasing market share of catalysts made of rare earth metals. For example, a single hybrid electric automobile requires around 10 kg of La in the form of trivalent lanthanides [202]. As such, the La market is expected to more than double by 2030 (USD$670 million) compared to 2023 (USD$303 million) (12.0% CAGR) [203], as shown in **Figure 3**.

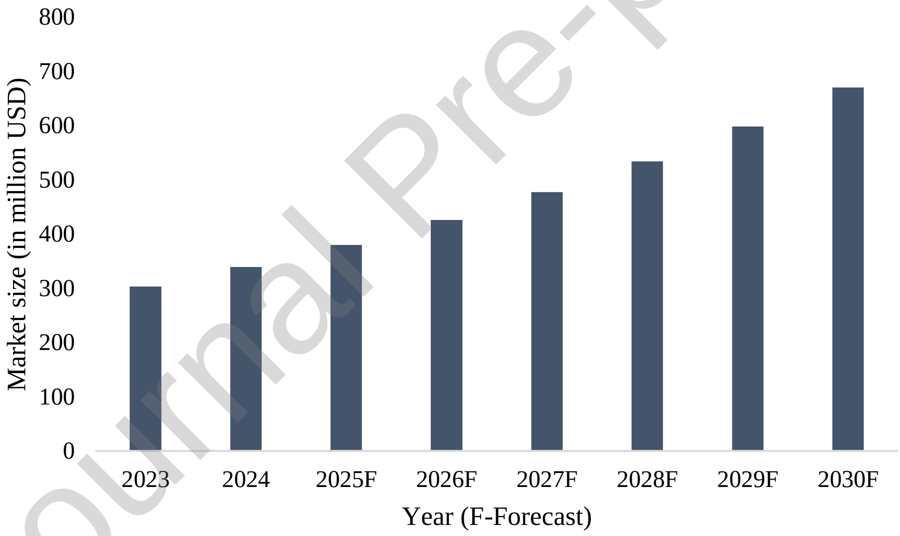

Figure 3: Global market size of La from 2023 to 2030 [203].

This growth trajectory is propelled by several factors, notably: i) the growing need for batteries in electric vehicles and in renewable energy storage solutions, ii) the expanding utilization of catalysts in the automotive and petroleum sectors, and iii) the growing demand for magnets in electronics and aerospace applications [204]. For context, according to Labchem (Pty) Ltd, the current (2025) selling market price for a piece of La (99.8% rare earth oxide, REO) in South Africa is R212.2 (USD$12.6) per gram. Furthermore, the Asia-Pacific region controls the worldwide La market, since resources in this area are relatively easily accessible [173]. Nonetheless, due to the existence of numerous metal processing plants, the industry has become extremely competitive [205] as a large number of industries use La, with China (~150 kt of apparent consumption of rare earth oxides in 2020) being the main player followed by Japan, USA, and the EU [206]. The recent geopolitical shifts surrounding REEs, whereby reliance on Chinese exports is projected to decrease, implying that the North-American market would likely rapidly expand [202].

5.2.2 Cerium

Ce is the most abundant REE in the Earth's crust and is a pliable metal with a gleaming grey hue [198]. It belongs to the lanthanide group and is highly reactive [207]. It can be found in several minerals, such as allanite (also known as orthrite), monazite, bastnasite, cerite, and samarskite, with Brazil, India, and Southern California, USA having the world's substantial Ce reserves [208, 209]. Metallic Ce can be obtained through thermal reduction methods, while Ce is commonly employed in alloy manufacturing. The growing utilisation of Ce-oxide nanoparticles in a variety of applications (e.g., gas sensors, drug delivery, catalytic converters in automobiles, water treatment and ceramic additives) [210], along with the increased focus on nanotechnology, are driving the growth in Ce market size. Specifically, as illustrated in **Figure 4**, the global market size for Ce was estimated to be worth USD$260 million in 2021, and this is projected to grow steadily (4% CAGR), reaching USD$341 million by 2028 [211]. For context, in South Africa, the current (2025) selling market price for cerium ingot (99.8% REO) is R110.1 (USD$6.5) per gram, according to quotation from Labchem (Pty) Ltd.

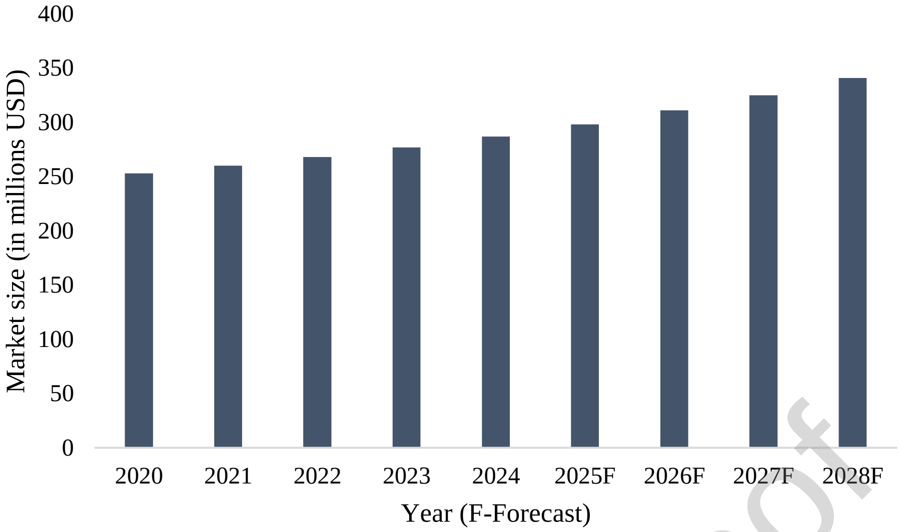

Figure 1*:* Global market size for cerium from 2020 to 2028 [211].

5.2.3 Neodymium

Nd is a silvery-white, slightly bendable metal that readily tarnishes when exposed to air and moisture. It is a member of the lanthanide series and is used in the manufacturing of several materials, such as coloured glass, magnets for electric vehicles and in magnetic resonance imaging (MRI) scanners [200], while Nd salts are also used to colour glasses and enamels. Renowned for its exceptional magnetic properties and resilience to extreme temperatures, Nd primarily serves as a component in permanent magnets. Consequently, the increasing demand for neodymium ferrous boron (NdFeB) permanent magnets from the automotive and electronics sectors is set to propel market expansion [212]. Moreover, technology advances in electric motors and the increasing adoption of NdFeB in the healthcare domain will further drive market growth [213].

Specifically, during the COVID-19 pandemic, the market encountered significant disruptions where various countries across the world implemented trade restrictions and transportation limitations. Such disruptions led to a sharp decline in Nd demand. As a result, an almost five-fold increase, from just over USD$1 billion to even nearly USD$5 billion, was observed between 2020 to 2022 and thereafter a steady growth (~7% CAGR) is expected with the global Nd market forecasted to increase to USD$7297 million by 2030 (**Figure 5**), with magnets manufacturing mainly being behind this market growth [213]. For context, in South Africa, the current (2025) selling market price for neodymium ingot (99.1% metal basis) is R180.6 (USD$10.7) per gram, according to quotation from Labchem (Pty) Ltd.

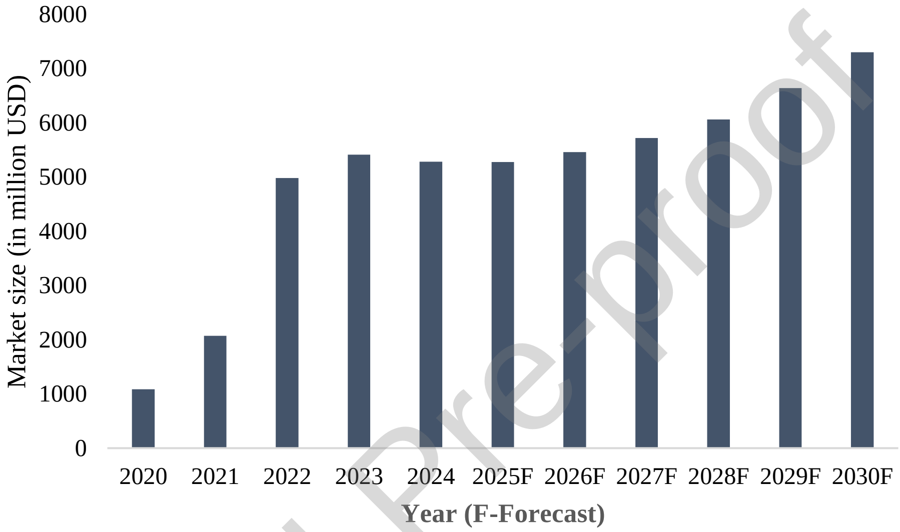

Figure 5: Global market size for Nd between 2020 to 2030 [213].

5.2.4 Gadolinium

Gd is a soft, silvery metal that also readily reacts when exposed to oxygen and water. It is used in alloys and particularly in magnets, electrical parts, data storage devices [214]. For example, Fe and Cr alloys can be made more functional and more resistant to oxidation and high temperatures when as little as 1% of Gd is added [215]. Furthermore, Gd compounds can be use as contrast agents, for enhanced MRI visualisation due to its unique magnetic properties [216]. It is also used in the core of nuclear reactors because of its superior neutron absorption capabilities [217]. As such, the primary drivers of Gd market growth (**Figure 6**) include modern medical imaging, green energy applications, use in alloys and electronics, and nuclear reactors (particularly in Japan and China).

In more detail, Gd global market is expected to grow from USD$1,535 million in 2024 to USD$ 2,510 million in 2030 (~9% CAGR) [218]. Geographically, the Gd market is currently dominated by the North America region due to the dense network of medical care centres that make use of advanced healthcare equipment and infrastructure, such as MRI and magnetic resonance angiography (MRA), which make use of Gd [219]. For context, in South Africa, the current (2025) selling market price for a piece of Gd (99.9% REO) is R423.7 (USD$25.1) per gram as per Labchem (Pty) Ltd quotation.

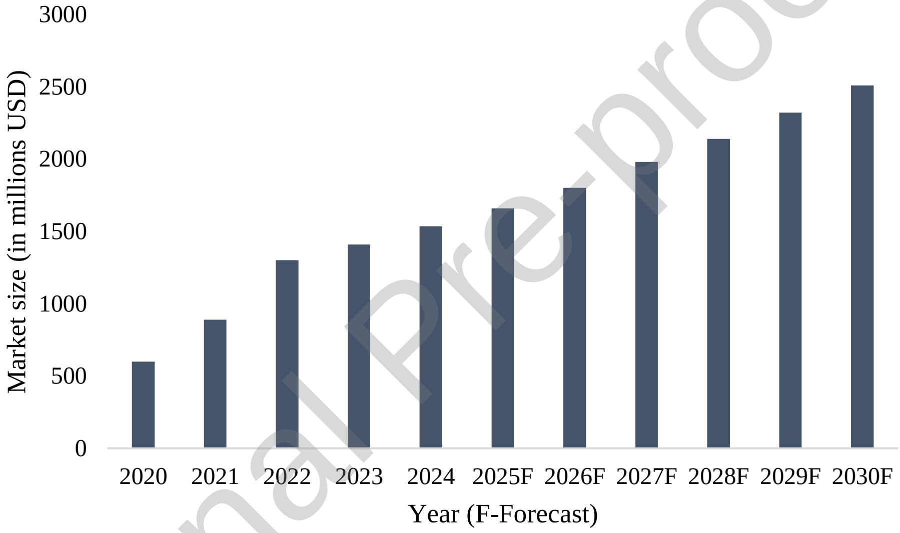

Figure 6: Global market size for Gd between 2020 to 2030 [218].

5.2.5 Yttrium

Y is a ductile, soft, silvery-white metal that frequently coexists with other lanthanides, as it seldom occurs in nature as an isolated element. This metal is usually employed in LEDs and red phosphors and is also utilised to improve the properties of electrodes, electronic filters, electrolytes, superconductors, lasers, numerous medical applications and tracing materials. The demand for high-temperature refractories (such as compounds that require stability at high temperatures) and petrochemical refineries has been reported to be the main drivers behind its strong market growth [220]. In more detail, a very high (~18%) CAGR has more double the Y market between 2020 and 2025, with this pattern expected to continue (**Figure 7**), leading to a USD$270 million market in 2027 from just USD$83 million in 2020 [221]. China is the largest producer and user of Y in the world, accounting for more than 40% of consumption in the Asia Pacific region alone, since the region has a significant amount of REE reserves [222]. In 2019, the leading exporters of Y-based materials were China, Thailand, Japan, and Australia, while Netherlands and United States of America were also reported to be amongst the largest exporters [223]. For context, in South Africa, Y ingot (99.9% REO) current (2025) market price is R439.6 (USD$26.1) per gram as per the quotation from Labchem (Pty) Ltd.

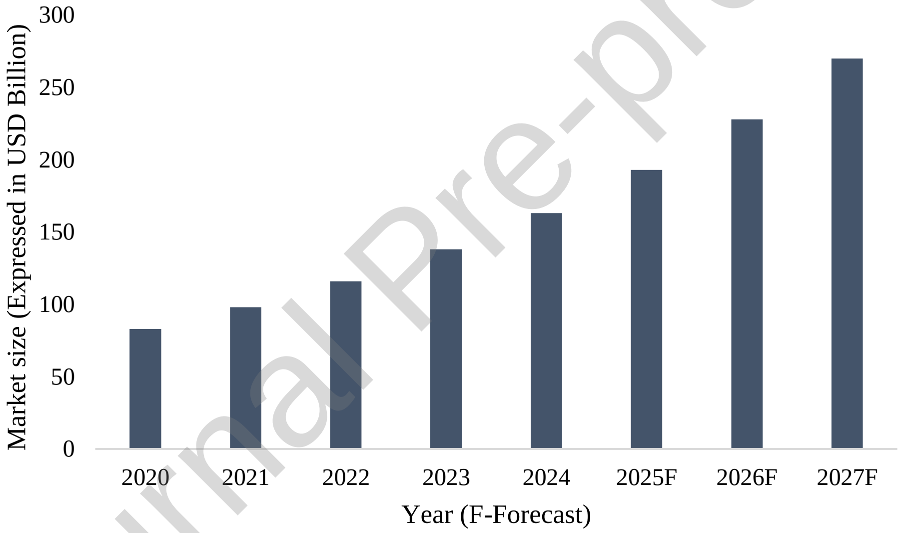

Figure 7: The global market size for Y between 2020 and 2027 (forecast) [221].

5.2.6 Dysprosium

Dy is a soft, silvery, glossy metal that is relatively stable in air at ambient temperature. It produces a wide range of colorful salts, but it can quickly dissolve in acids. Dy is used in nuclear reactor control rods, due to its strong thermal neutron absorption cross-section [224]. When combined with Cd, it can be utilized to generate infrared radiation [225] and can also be used in applications such as sonar systems, sensors, transducers, data storage (compact discs, hard disks), lasers, and phosphor activators [226]. The market size for Dy has seen significant fluctuations, as the market steeply increased from USD$490 million in 2020 to USD$790 million due to supply chain disruptions, thereafter a market correction is observed as supply was stabilized and then a stable future growth is expected, with the market expected to reach USD$786 million in 2030 [227] (**Figure 8**). Projections indicate a substantial growth trajectory for the global Dy market, largely fuelled by demand from both the automotive and electronics industries, as well as the healthcare sector [228]. Moreover, the expanded application of permanent magnets in consumer electronics, such as smartphones, televisions, and loudspeakers, further amplifies the demand for Dy worldwide [229]. Notably, the Asia-Pacific region, particularly China, emerges as the primary market leader for Dy [230]. For context, in South Africa, the current (2025) market price for dysprosium ingot (99.8% REO)) is R183.8 (USD$26.1) per gram according to quotation from Labchem (Pty) Ltd.

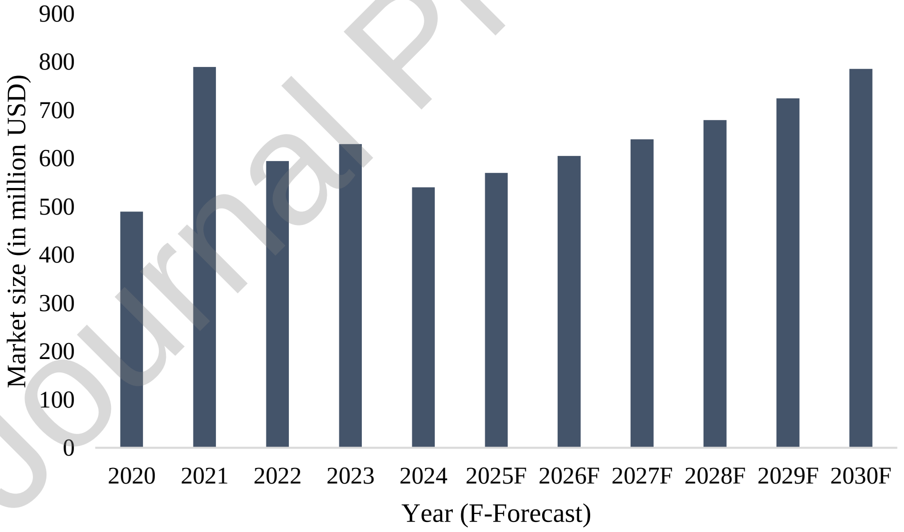

Figure 8: The global market for Dy from 2020 to 2030 [227].

5.3 Factors affecting the rare earths market growth

5.3.1 Increasing demand and limited supply

REEs are crucial elements that are necessary in a wide range of high-tech applications, including electronics, renewable energy, electric cars, defence systems, and advanced manufacturing [231]. This rising demand is primarily apparent for elements utilised in wind energy and electric vehicles, such as Dy and Nd [232]. The growing demand for REEs in these technologies and industries is driving the need for a steady supply of such elements. Recycling and recovery of REEs from secondary sources, including mine wastewater streams, has become paramount to alleviate the shortage of supply [78].

Furthermore, although relatively common in the Earth's crust, REEs are often widely distributed but seldom exist in concentrated mineral deposits [104]. Their mining is also challenging as they occur in complex ores and low concentrations [20], and therefore is associated with high cost, environmental pollution, and even geopolitical issues [233]. As such, secondary sources such as AMD present an alternative source for REEs that can potentially supplement or possibly replace, to a certain extent, conventional supply.

5.3.2 Government support and regulations

Across the world, various countries are advocating for the implementation of circular economy, sustainable resource management, resource security and strategic autonomy [174]. This is in line with efforts to introduce waste-to-resource paradigms through the extraction and use of REEs from alternative sources such as AMD [234, 235]. The market for REEs generated from AMD may be stimulated by financial incentives, research fundings, and supportive regulatory frameworks [236]. Specifically, current and future revenue mix pertaining to REEs is influenced by trends and disruptions linked to producers and consumers [237]. The REEs market is expected to grow significantly due to demand in electric vehicles and wind turbines, in light of the international frameworks to curb carbon emissions, such as from internal combustion engines [238, 239]. Furthermore, the fourth industrial revolution (4IR) has been projected to greatly rely on the use of phosphors made from REEs [240]. The benefits encompass faster product innovation, long-term contractual agreements between producers and consumers, and access to green tax incentives from governments.

6 Conclusion and future research directions

AMD contains a variety of metals, oxyanions, and other dissolved chemical species, which can greatly affect receiving environments but can also be recovered using different techniques, thus promoting circularity and sustainability. Common technologies used for the recovery of valuable materials from AMD include ion exchange, adsorption, precipitation and solvent extraction, while for water reclamation membrane technologies are often employed, with both advantages and shortfalls for consideration. AMD composition, which is governed by the geology of the mined ore and downstream areas, will define the resources that can be recovered, which typically include metals such as Fe and Al, sulfuric acid, and water. Recently, research has also focused on recovering REEs from AMD, given their importance in many industrial applications and their strong and growing market. Specifically, the global REEs market was estimated at approximately USD$5.9 billion in 2023 and is anticipated to reach USD$14.2 billion by 2033, having a 12% CAGR. Furthermore, the market shares for La, Nd, Gd, and Dy are projected to be approximately 670, 7297, 2510, and 786 USD$ million, respectively, in 2030, and their respective CARGs to be 12%, 7%, 9%, and 7%, respectively. On the other hand, the market share for Ce is estimated to reach USD$341 million in 2028 at 4% CARG, while Y is projected to reach USD$270 million at 7% CARG. Although La and Ce are the most abundant REEs in the Earth’s crust, they are only employed in a few specific applications, and the demand for other REEs, particularly Nd used in permanent magnets, is growing despite their lower prevalence. This market analysis can improve the knowledge base on the market shares of REEs recovered from AMD, their respective CAGR, market drivers and applications. Overall, this review deciphers the critical aspects of AMD, from a problem to a solution, hence closing the loop of the circular economy and ensuring ecological sustainability.

Based on the distilled findings of this literature review, insights on the recovery of valuable minerals from AMD place emphasis on the need to integrate conventional technologies with novel techniques that are emerging in the water landscape to improve the recovery process. Furthermore, emerging research should also demonstrate ZLD processes and closed-loop systems. Such systems could also use advanced hybrid treatment or sophisticated oxidation techniques that integrate chemical, biological, and physical techniques to effectively and comprehensively treat AMD to improve metal recovery from AMD and break down complex pollutants. Furthermore, it is also recommended to explore the cross-linking mechanism of feed materials in the recovery process to avoid leaching of toxins back into the environment, along with innovating and applying high surface area nanoparticles with high mechanical stability and containing customized functional groups to selectively adsorb and recover particular metals and metalloids from AMD. In light of the energy crises in the developing world, the possibility of treating AMD and recovering energy at the same time by using bio-electrochemical systems (BES) can be investigated, including microbial fuel cells and microbial electrolysis cells, as this would also offset the operational costs and serve as an avenue of economic benefit. The 4IR has penetrated the research space, hence pollution modelling and algorithms with hydrogeological and geochemical datasets for baseline and mitigation scenarios would help forecast AMD composition and impacts, and optimize treatment procedures, ultimately informing policy development on AMD mitigation and environmental sustainability. This will also aid in the optimisation of recovery and beneficiation operations to enhance efficiency and reduce operational costs. Along this scope, quantum chemistry for chemical calculations and molecular dynamics simulations can be applied to understand the fundamental reaction mechanisms involved in AMD treatment and metal recovery at the atomic level, as well as computational chemistry to design novel ligands and chelating agents that can selectively bind and recover target metals from AMD.

Notably, a thorough techno-economic analysis can also evaluate the practicality and financial sustainability of state-of-the-art AMD recovery and treatment methods, as well as establish research and development (R&D) initiatives that explore technology that will reduce or combat the co-extraction of impurities with the targeted REEs from AMD. Noting the importance of REEs and other minerals, a circular economy (CE) business model can be developed for REEs and other valuable minerals recovered from AMD in the treatment plants. Since AMD is a valuable source of minerals that can be beneficiated and valorised into crucial materials, there is a need for the government to provide support and incentives to AMD treatment plants, as this will also assist in the beneficiation of their waste, while giving back to the economy of the country.

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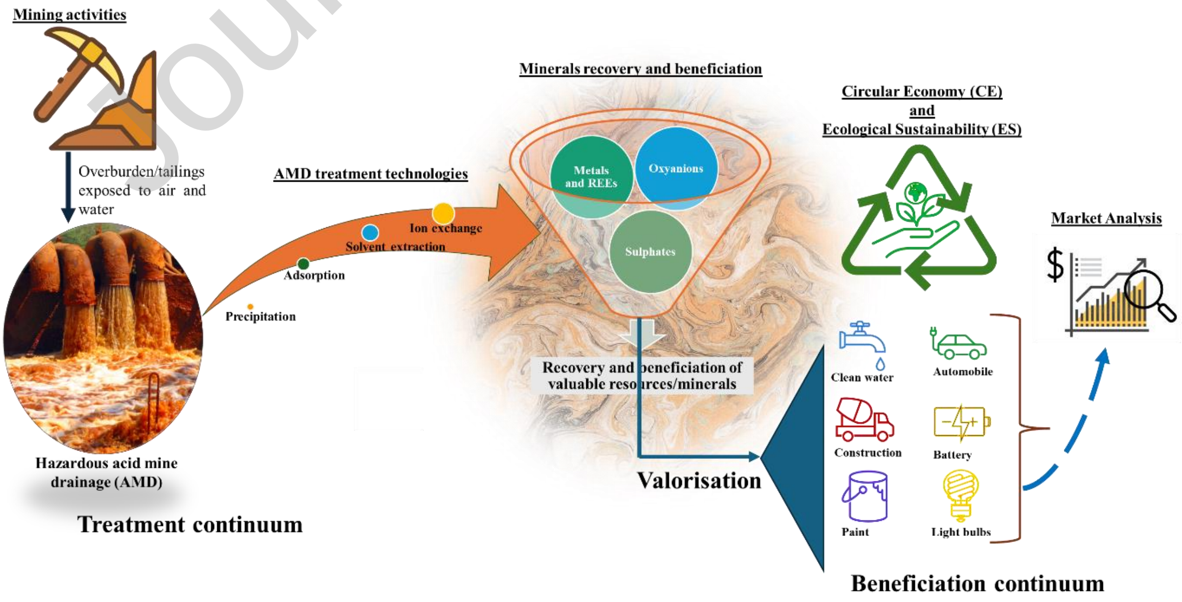
Declaration of Competing Interest

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships, which may be considered as potential competing interests:

There is no conflicts of interest observed between the authors of this manuscript. All the authors have read and approved the manuscript.

Graphical abstract



Highlights

- This paper successfully reviewed recent updates on acid mine drainage beneficiation.
- Progress in knowledge and hindering factors on acid mine drainage treatment were highlighted.
- Pragmatic applications in minerals recovery, reclamation and valorization were explained.
- Avenues for future research outlooks and needs were also underpinned in this paper.